



Quantifying global exergy resources

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Abstract

Exergy is used as a common currency to assess and compare the reservoirs of theoretically extractable work we call energy resources. Resources consist of matter or energy with properties different from the predominant conditions in the environment. These differences can be classified as physical, chemical, or nuclear exergy. This paper identifies the primary exergy reservoirs that supply exergy to the biosphere and quantifies the intensive and extensive exergy of their derivative secondary reservoirs, or resources. The interconnecting accumulations and flows among these reservoirs are illustrated to show the path of exergy through the terrestrial system from input to its eventual natural or anthropogenic destruction. The results are intended to assist in evaluation of current resource utilization, help guide fundamental research to enable promising new energy technologies, and provide a basis for comparing the resource potential of future energy options that is independent of technology and cost.

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1. Introduction

All activity in the universe derives from matter and energy becoming more disorganized as expressed by the second law of thermodynamics. This law can be used to quantify the degree of disorder and define the work potential of a substance relative to a reference state. When the substance is allowed to interact only with a reservoir in the reference state, this work potential is the exergy of the substance [1]. Exergy describes the quality of energy in addition to the quantity, providing deeper insight into work potential than analyses which only utilize the first law.

Exergy exists in many different types of reservoirs from chemical potential stored in hydrocarbon bonds to the kinetic energy of the wind. Humans access and process exergy in these reservoirs in order to provide energy services. Exergy does not describe the ability of humankind to exploit a resource, but is a path-independent property, serving as a model for the theoretically extractable work contained in a resource regardless of geometry, technology, and economics. This independence makes exergy a useful tool for evaluating the efficiency of resource energy conversion and comparing the magnitudes of resources both within and beyond current technical ability and experience [2].

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Nomenclature

a	area (m ²)
A	wave amplitude (m)
c_p	specific heat capacity (J/kg K)
E_b	radiation energy flux (W/m ²)
$\Delta_f g, \Delta_R g$	Gibbs free energy of formation (f), reaction (R) (J/kg)
$\Delta_D h, \Delta_R h$	specific enthalpy of dissociation (D), reaction (R) (J/kg)
m	mass (kg)
\dot{m}	mass flow rate (kg/s)
P	pressure (Pa)
R	specific gas constant (J/kg K)
Δ_{R^S}	entropy change of reaction (J/kg K)
s	specific entropy (J/kg K)
t	period (s)
T	temperature (K)
u	specific internal energy (J/kg)
v	specific volume (m ³ /kg)
V	velocity (m/s)
ν_e	electron neutrino
$\bar{\nu}_e$	electron antineutrino
X_0	subscript 0 denotes property X at the reference state
y	mole fraction
z	vertical distance above reference height (m)
Z	compressibility factor
μ	specific chemical potential (J/kg)
ψ	specific exergy (J/kg)
Ψ	exergy flux (W, W/m, W/m ²)
ρ	density (kg/m ³)
Π	osmotic pressure (Pa)

The paper begins with a brief summary of exergy theory. This background will serve to motivate the present perspective on resources and provide direction for calculating the major types of exergy used in the study. While the evaluation of exergy is independent of technology, the exergy reservoirs selected for this study are either currently in use or on the technological horizon. This paper will identify the primary exergy reservoirs that feed the secondary resources we exploit, and classify these resources as either non-renewable or renewable based on their time scale of replenishment. The extensive exergy of these resources and their interconnecting fluxes will be quantified, with the supporting intensive exergy derivations provided in Appendix A.

2. Exergy method

Exergy analysis provides a method to evaluate the maximum work extractable from a substance relative to a reference state [1]. This reference state is arbitrary, but for terrestrial energy conversion the concept of exergy is most effective if it is chosen to reflect the environment on the surface of the Earth. The various forms of exergy are due to random thermal motion, kinetic energy, potential energy associated with a restoring force, or the concentration of species relative to a reference state. Temperature reflects a combination of the random translational, rotational, and vibrational energy of non-distinct, atomic-scale bodies. Kinetic energy is associated with the bulk motion of a distinct body or net large-scale motion of a fluid. Potential energy arises in many forms due to the different types of forces in nature. The gravitational, electromagnetic and the two nuclear forces each define a type of potential energy. The degree of physical disorder relative to the reference

state has work potential, but is usually small. This exergy metric usually describes the concentration of species in a mixture and is included in chemical exergy. We extract work by changing the properties of these motions and potentials through energy and matter exchange with large reservoirs in the environment.

2.1. The reference state

In order to establish how much work potential a resource contains, it is necessary to compare it against a state defined to have zero work potential. An equilibrium environment which cannot undergo an energy conversion process to produce work is the technically correct candidate for a reference state. The reservoirs of the reference state must be large enough such that their properties are not changed by the required interactions over the time scale of the exchange. The Earth's atmosphere, ocean and crust are often defined as such a state for practical analysis, even though these environments are not in equilibrium due to access and kinetics barriers, such as atmospheric oxygen's access to metals in the crust. In addition, the reservoirs comprising the environment cannot necessarily be considered large, as anthropogenic activities alone are on such a scale that they have altered the atmospheric concentration of carbon dioxide. Approximations can be made using a model of the environmental chemical reference state reflecting chemical properties and concentrations found in different sectors of the environment [3,4]. The following sections summarize the major forms of exergy and provide formulas on which to base exergy calculations for a specific resource.

2.2. Physical exergy

We include the thermal, mechanical, kinetic, and gravitational potential energy of a substance when calculating physical exergy. Physical exergy provides the maximum amount of reversible work that can be produced by bringing the temperature, pressure, velocity, and position within a gravitational field into equilibrium with the defined reference state. Combining the first and second laws of thermodynamics gives the physical exergy of a stream

$$\psi_{ph} = [h - h_0 - T_0(s - s_0)] + \frac{(V - V_0)^2}{2} + g(z - z_0). \quad (1)$$

The classical thermodynamic properties grouped within the brackets are well documented for many substances and mixtures in a wide range of states. The second and third terms are a result of measured position and velocity relative to the reference state and their exergy and energy contents have the same numerical value.

2.3. Chemical exergy

Electrostatic bond energy and species concentration relative to the chemical reference model of the environment form the basis of chemical exergy. Chemical exergy is defined in terms of the sum of chemical potentials of the component species

$$\psi_{ch} = \sum_i y_i \mu_{ch_i}^0. \quad (2)$$

The chemical potential μ_{ch}^0 is due to the Gibbs free energy of reaction of a substance undergoing a chemical reaction with reference species and concentration relative to reference species in the environment as given by

$$\mu_{ch_i}^0 = -\Delta_R g^0 + RT_0 \ln\left(\frac{y_i}{y_0}\right). \quad (3)$$

The change in Gibbs free energy of reaction reflects the net energy release from chemical bonds and entropy change accompanying a reaction with reference species represented by

$$\Delta_R g^0 = \Delta_R h - T_0 \Delta_R s, \quad (4)$$

where the enthalpy change of reaction is the difference between the commonly tabulated enthalpies of formation of the reactants and products.

The exergy due to species concentration differences in most chemical fuels is much less than the exergy of the chemical bonds. Concentration exergy is due to the relative abundance of species in a substance compared with the average concentration of those species in the reference state. Since concentrations of various atoms and molecules vary widely on Earth depending on location, an exact, universal determination of concentration exergy is impossible. Tables of standard chemical exergy for many different types of species accounting for Gibbs free energy and an approximation of terrestrial concentration exergy aid in this calculation [4].

2.4. Nuclear exergy

The change in potential energy associated with the strong and weak nuclear forces during a nuclear reaction determines nuclear exergy [5,6]. The strong force is responsible for holding nucleons together despite the mutual electrostatic repulsion of protons. The weak force releases its potential primarily through conversion of neutrons into protons during the process of beta decay. As nuclides undergo exothermic nuclear reactions, the potential energy due to the strong and weak force is reduced, forming products with less rest mass than the reactants and releasing energy. This mass difference is directly proportional to the “bound energy” released, as described by Einstein’s mass and energy equivalence. Much like the Gibbs free energy in a chemical reaction, the difference in bound energy between nuclear products and reactants is equivalent to the reactant exergy

$$\psi_{nuclear} \approx \frac{(\sum m_{i,p} - \sum m_{i,r})c^2}{\sum m_{i,r}}, \quad (5)$$

where c is the speed of light, if the reference state is selected such that the products cannot be utilized further. The change in entropy and concentration of products relative to the environment are both negligible for the reactions we will consider. Non-conservation of species and the production or requirement of excess subatomic particles prevents a standard exergy for each nuclide in a form similar to chemical species standard exergy.

Nuclides have specific bound energies [7] following a curve rising on either side of the atoms in the iron family of the periodic table as shown in Fig. 1. Bound energy is proportional to the mass difference between a nuclide and the constituent particles comprising a nuclide relative to the most stable nuclide known, Ni-62, defined to have zero bound energy. Heavier atoms such as uranium can undergo fission while fusion can occur between lighter atoms such as isotopes of hydrogen. The difference in specific bound energy between reactants and products of a nuclear reaction approximates the exergy release of the reaction. Similar to hydrocarbons chemically reacting with oxygen to produce low Gibbs free energy carbon dioxide, the relatively low bound energy of He-4 provides the fusion of hydrogen isotopes a high specific exergy.

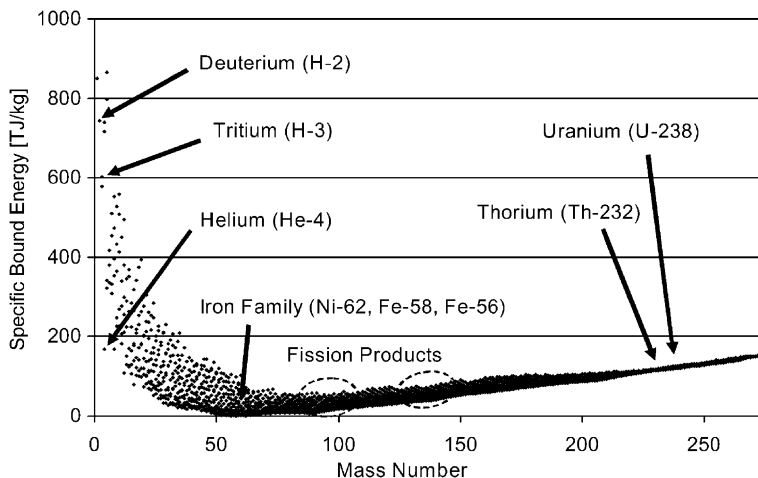


Fig. 1. Nucleus-bound energy of known nuclides (Ni-62 = 0).

Nuclear reactions in stars involve a wide range of nuclides [8]. In the future, our technology may be able to mimic these processes and utilize a wider range of materials for nuclear energy conversion. However, in order to remain within the horizons of the energy conversion technologies of the near future, this study only considers naturally occurring nuclides involved in currently proposed nuclear cycles: U-235, U-238, Th-232, H-2, Li-6 and Li-7. The products of these cycles are assumed to have zero nuclear exergy. An additional correction to keep this study limited to near-future technical feasibility will be to exclude the energy of neutrinos released from the fission of heavier elements. Neutrinos account for about 5% of the energy released during fission, but only mildly interact with other matter through gravity and the weak nuclear force [7,8].

3. Exergy reservoirs and flows

All activity on Earth derives from four primary reservoirs of exergy that have existed since the formation of the solar system: fusible atoms in the Sun, fissionable atoms on Earth, the thermal energy of the Earth's interior, and the gravitational potential energy and relative kinetic energy of celestial bodies. The exergy from these reservoirs accumulates through natural processes in a wide variety of secondary reservoirs. These secondary reservoirs can either be classified as terrestrially finite or renewable depending on the rate at which they are replenished. Table 1 illustrates this decomposition between primary and secondary exergy reservoirs and provides an approximate time constant for resource replenishment as a means for distinguishing renewable from non-renewable resources.

The solar nuclear reservoir is the largest and transfers exergy to an array of secondary reservoirs. Many of these solar-derived secondary reservoirs are not independent; large-scale utilization of one could change the magnitude or properties of others. Ocean tidal dissipation results primarily from the gravitational coupling that transfers the rotational kinetic energy of the Earth to the gravitational potential energy of the Moon. Thermal energy from the Earth's original gravitational collapse, deep radionuclide decay, and solid Earth tides comprise the geothermal resource. The surface terrestrial nuclear reservoir does not transfer exergy across the boundary of our sphere of influence, but is on a scale comparable to other primary reservoirs if deuterium fusion cycles are included.

The cascading flow of exergy from these primary reservoirs into secondary reservoirs and on to its eventual natural or anthropogenic destruction can be summarized as a system of exergy reservoirs and flows. Fig. 2 illustrates the portion of this system within our terrestrial sphere of influence. Exergy flow is represented by paths ending in areas of natural exergy destruction or arrows representing anthropogenic usage for energy services. Anthropogenic exergy destruction of resources is defined as the total amount of exergy destroyed

Table 1
Resource classification and replenishment time scale

Exergy reservoirs by class			Replenishment time scale
Primary	Approximate size	Secondary (resources)	
Solar nuclear	8E43 J	Radiation exchange	Milliseconds
	Total radiant ^a	Wind and wave	Hours
	4E34 J	Precipitation	Days
	Earth incident ^a	Biomass	Years
		Ocean thermal gradient	Hundreds of years
		Fossil fuels	Millions of years
Celestial bodies	5E29 J Earth rotational KE	Tidal	Hours
Earth thermal	2E31 J thermal ^b	Geothermal	Days–years
Terrestrial nuclear	1E31 J deuterium	Nuclear materials	None

^aSum of radiation exergy flux over a lifetime of 5 billion years.

^bEstimate of the geothermal energy reservoir assumes 2800 K average mantle and core temperature, mantle and core average specific heat 6.25E27 J/K [9] (1.4 E21 J), and assumed average radionuclide contribution of 20 TW for 5 billion years (0.3E21 J). The solid Earth tide contribution is small [10].

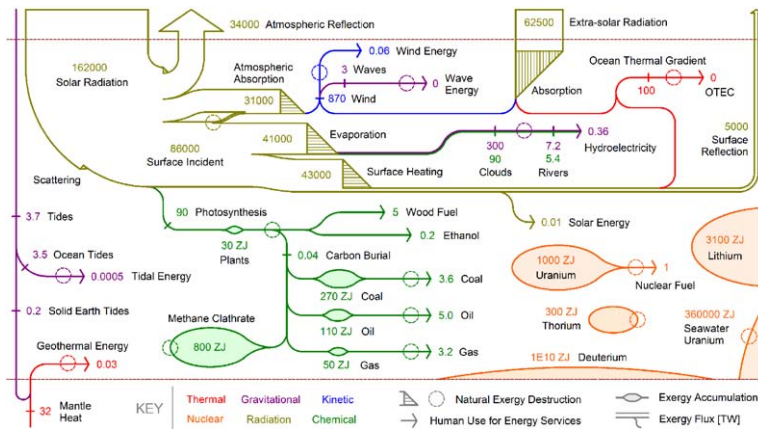


Fig. 2. Global reservoirs, flux, and anthropogenic destruction of exergy.

while processing or attempting to collect a resource, regardless of the amount of useful work extracted. Unlabeled, dashed circles along these paths represent natural exergy destruction processes such as friction and chemical or nuclear decay that are small compared to the natural destruction modes of cosmic radiation exergy (hatched areas). The color of the exergy flow or reservoir corresponds to the predominant type of exergy it contains. When a single resource comprises multiple types of exergy, separate quantifications are present in the appropriate color. The ovals illustrate accumulations of exergy within the human sphere of influence.

The estimations of extensive exergy reservoirs and flows contained in Fig. 2 have been calculated using the intensive exergy values developed in Appendix A. The following sections break down Fig. 2 by resource domain, provide the data and assumptions comprising the presented values, and summarize the results of Appendix A.

4. Exergy of renewable resources

4.1. Cosmic radiation exchange

Cosmic radiation is the largest exergy input to the terrestrial system and drives most activity on Earth. Exergetic radiation crosses the top of the stratosphere either in the form of high-temperature solar radiation or low-temperature extra-solar radiation. Earth's distance from the Sun gives it a moderate temperature, providing work potential relative to both the hot surface of the Sun and cold space.

Even though the Sun is relatively small in our sky, the large temperature difference between the surfaces of the Earth and Sun provides a larger exergy input than extra-solar radiation exchange. Estimates of the fate of solar radiation exergy [11,12] are combined with the exergy penalty associated with diffusive scattering to obtain the present values for exergy flow and destruction. As solar radiation enters the terrestrial environment, it is reflected or absorbed. This analysis assumes 25% of the solar radiation passing through the atmosphere [13] and 100% of reflected radiation becomes diffuse with a corresponding drop in energy quality [14]. Absorption causes the radiation to undergo energy conversion to either low-quality thermal energy or chemical energy through photosynthesis. Of the 162 PW solar radiation exergy reaching Earth, 42 PW are immediately reflected and scattered in the upper atmosphere, leaving a stream of 34 PW radiating back into space. Once the radiation enters the atmosphere, a complex series of reflections and absorptions take place. Assuming a single reflection off the Earth's surface and that the same fraction of reflected radiation off the surface is absorbed in the second pass though the atmosphere as the original incoming radiation, approximately 86 PW exergy is incident on the surface of the Earth. Overall, of the 120 PW entering the lower atmosphere, 31 PW are converted to thermal energy in the atmosphere, 38 PW becomes thermal energy in the

land and ocean, 41 PW contributes to evaporating water, and 5 PW diffuse radiation is reflected off the surface and escapes into space.

While radiation exchange between the Earth and Sun adds both energy and exergy to the terrestrial environment, the net flow of energy and exergy are opposite for the extra-solar radiation exchange. The low-temperature radiation permeating space in the vicinity of our solar system serves as a cold sink for our relatively warm planet, driving the transfer of 122 PW long-wave radiation energy from the terrestrial environment into space with an accompanying net input of 63 PW exergy.

Solar radiation originally has an average exergy density of approximately 1270 W/m^2 [12]. The exergy reaching the surface depends heavily on latitude and average local cloud cover. A global average of the remaining solar radiation at the surface gives 168 W/m^2 [15]. Low-temperature, extra-solar radiation including the microwave background radiation at 2.73 K has a very high ratio of exergy to energy. Subtracting the exergy of outgoing long-wave radiation relative to the reference temperature of 289 K from the extra-solar radiation exergy flux, the net average exergy density due to extra-solar radiation exchange at the outer edge of the stratosphere is about 121 W/m^2 . The amount of exergy converted or destroyed on solar collectors currently totals about 1 GW on photovoltaic panels and 15 GW on solar thermal panels [16].

4.2. Wind

Wind potential and kinetic energy derive from pressure differences caused by the uneven heating and cooling of the atmosphere. It has been estimated that 870 TW of the cosmic radiation exergy absorbed at the Earth's surface and in the atmosphere is transferred to wind kinetic energy and dissipated as friction [17]. Friction within the surface boundary layer dissipates approximately one third of this exergy, while the remainder is dissipated through viscous friction in free stream atmospheric flow [18]. Wind speeds are heavily influenced by surface characteristics and features, but generally increase with altitude.

The average global wind speed at 50 m of 6.60 m/s [15] has an exergy of about 336 W/m^2 perpendicular to the wind direction, assuming a Weibull distribution [19] with a shape factor of 2 and a scale factor of 7.45. The amount of exergy converted or destroyed at collectors worldwide is about 60 GW [20].

4.3. Ocean surface waves

As the wind blows over the ocean, it transfers momentum to currents and surface gravity waves totaling an estimated 60 TW [21]. Open ocean surface wave breaking and internal friction reduces the surface gravity wave exergy flow to 3 TW breaking on the world's coasts. The average specific exergy of surface waves ranges from 10 to 100 kW/m, with much higher values during storms [22]. Many wave energy conversion systems have been proposed, but none are currently in large-scale use.

4.4. Precipitation

A portion of the 41 PW solar radiation contributing to the evaporation of water remains as about 300 TW gravitational and 90 TW chemical exergy flow in the clouds, assuming an average water vapor height of 1.7 km. The chemical exergy component is due to the salinity difference between freshwater and the ocean. On average, about 18 Tg/s water precipitates to the Earth's surface [23]. Of this total, 3.9 Tg/s falls on land or ice to an average surface height of 670 m for a remaining exergy flux of 25 TW gravitational [24,25] and 19 TW chemical. Plant transpiration allows 2.0 Tg/s freshwater to re-enter the atmosphere [26]. The remaining 1.9 Tg/s does not pass through plants, of which about 0.4 Tg/s evaporates and 1.5 Tg/s enters the oceans as a liquid. The exergy of the 1.1 Tg/s precipitation that reaches the ocean through the world's major rivers [26] is about 7.2 TW gravitational and 5.4 TW chemical.

The gravitational exergy of freshwater at the precipitation-weighted average elevation is 6.57 kJ/kg and the chemical exergy is 4.9 kJ/kg relative to an average ocean salinity of 35 ppt [27]. About 400 GW of the gravitational exergy flow of freshwater is converted or destroyed in our collectors [16]. No large-scale efforts are currently underway to convert the chemical exergy of freshwater.

4.5. Biomass

Of the 86 PW solar radiation exergy incident on the land and oceans, approximately 10–20 PW falls on plants and algae. Converting sunlight to chemical exergy through photosynthesis at about 0.5–1.0% average efficiency [28], plants and algae have a net productivity of about 90 TW, with 65 TW on land [29] and 25 TW in the ocean [30]. These flows feed reservoirs of 30 ZJ biological matter on land and 0.15 ZJ in the ocean [28], reflecting an average biomass residence time of 10 years and 1 month, respectively [31].

The specific exergy of biomass ranges from 15 to 20 MJ/kg on a dry basis, depending on carbon and ash content. Woody biomass tends to have higher carbon content, while marine biomass often has high ash content. Humans appropriate about 16 TW of the land productivity [32], of which about 5 TW contributes to the consumption of 1.5 TW in the form of wood fuel [33] and approximately 0.2 TW goes into the production of 20 GW ethanol [16,34].

4.6. Ocean thermal gradient

The solar warming of seawater in the tropics and the radiative loss of thermal energy to space near the poles creates a density-driven current which circulates seawater from the surface to the deep ocean. The cold, more dense seawater sinks at the poles and travels to the deep tropics where it undergoes upwelling and warming once again. This cycle maintains a thermal energy gradient from the surface to the deep ocean. Taking the surface water as the reference state, the cold, deep water has a certain physical exergy. With a thermal energy transport of 2000 TW [35], an assumed average temperature difference of 20 K gives an exergy flow of about 100 TW transferred to the thermal gradient.

Due to the small temperature differential, the exergy density of the ocean thermal gradient is relatively small. A 20 K temperature difference gives a specific exergy of approximately 800 J/kg seawater. No significant conversion of this resource currently exists.

4.7. Tides

Tides are a result of gravitational field couplings between the rotating Earth and the Moon and Sun. The rotation of the Earth through the gravitational field gradients of the Moon and Sun causes motion on the surface of the Earth in response to portions of the Earth moving in and out of the areas of strongest gravitational attraction. Exergy associated with this motion dissipates as friction, decreasing the rotational kinetic energy of the Earth. It is estimated that 3.7 TW tidal energy is dissipated worldwide with 2.5 TW dissipation occurring in the shallow ocean and continental shelves, 1.0 TW in the deep ocean, and 0.2 TW as friction in the solid Earth [10,36,37]. The moon is responsible for 70% of the total dissipation.

Specific tidal exergy is equivalent to the gravitational potential energy due to the height difference between tidal maxima and minima over the tidal record. For a given range of time between inflection points, tides have a specific exergy of 10 kJ for each m² of reservoir and each m of height difference. Existing tidal-induced currents at geographical constrictions are another method of characterizing tidal exergy, using similar methodology to wind currents. The current exergy destruction from tidal energy collectors is about 500 MW [38].

4.8. Geothermal

Geothermal exergy derives from the decay of nuclides in the Earth's interior, the original heat from the gravitational collapse of the early Earth, and to a lesser extent dissipation of tidal forces in the solid Earth. While the nuclear materials generate approximately 30 TW thermal energy [39] and the solid Earth tidal dissipation is about 0.2 TW [10], it is not enough to balance the 45 TW conduction losses to the surface [40], allowing the Earth to slowly cool. The temperature of the Earth at depth varies widely depending on the geologic formations present in an area. Taking the temperature at the interface of the crust and the mantle at 40 km deep to be 1050 K [40], the flow of geothermal exergy into the crust is approximately 32 TW.

The specific exergy of a geothermal site depends on the temperature at the collector, the pressure and composition of fluid in the reservoir, and the ability of the surrounding rock or fluid to transport thermal energy to the collector. Utilization of a geothermal site often changes the thermal or fluid properties of the reservoir to a new equilibrium dependent on the method of energy extraction. The specific exergy of a representative brine at 436 K with a reference temperature of 286 K is 125 kJ/kg [41]. The amount of exergy destroyed or converted worldwide in geothermal collectors is about 25 GW for electricity generation and 3 GW for direct thermal use [16].

5. Exergy of finite resources

5.1. Fossil fuels

Approximately 40 GW biological matter is buried under sediment on an average ongoing basis [42]. An uncertain fraction of this flow is converted under heat and pressure to higher energy density fossil fuels. A small fraction of the fluid portion of these fossil fuels enters geologic traps where they are able to reside for millions of years without reaching the surface and oxidizing. The layers of solid fossil fuel such as coal and methane clathrates and geologic traps containing fluid fuels such as petroleum and natural gas constitute reservoirs of chemical exergy. Estimated occurrences of coal, petroleum, and natural gas total 270, 110, and 50 ZJ, respectively [43]. About 10 ZJ of the petroleum resource is in pure liquid form containing low molecular weight, volatile hydrocarbons, while the remaining 100 ZJ exist as heavier liquids or in mixtures with inorganics. While estimates of methane clathrate occurrences vary widely, a review among various authors suggests about 4 ZJ are stored in continental permafrost deposits and approximately 400 ZJ in ocean sediments [44].

The specific exergies of fossil fuel resources are similar, but vary primarily with carbon content and the percentage of inert components. Coal exists in a wide variety of grades. The specific exergy of coal increases with carbon content from about 20 to 30 MJ/kg. Humans currently convert 3.6 TW coal [45]. Low molecular weight petroleum has a chemical exergy from 40 to 44 MJ/kg. Higher molecular weight petroleum and the hydrocarbon portion of the inorganic mixtures have a chemical exergy close to 40 MJ/kg, but decreases to near 10 MJ/kg or less when the mass of the inorganic portion is included. The human use of conventional petroleum is about 5.0 TW [45], while unconventional petroleum use is about 0.1 TW [16]. Natural gas is a widely varying mixture of low molecular weight hydrocarbons, nitrogen, and carbon dioxide with several other trace species and has a typical specific exergy of 50 MJ/kg. Conversion of natural gas stands at 3.2 TW [45]. Methane clathrate is approximately 85% water [44], which reduces its specific exergy to about 4.8 MJ/kg. No commercial efforts are being made to extract and convert methane clathrate.

5.2. Nuclear materials

Uranium and thorium are two heavy elements created in stellar events billions of years ago that readily undergo nuclear fission and exist in significant abundance on Earth. These elements can be found throughout the crust, but are concentrated in certain geologic deposits. Concentrated uranium occurrences are estimated to be about 13 Tg [42], representing an exergy reservoir of 1 YJ with a specific exergy of 77 TJ/kg. The known 4 Tg thorium resource has an exergy of 300 ZJ [46] with a specific exergy of 78 TJ/kg. In addition to ores, uranium also exists at a concentration of 3.3 ppb in the ocean [47]. With approximately 1.4 Yg seawater, the seawater uranium exergy reservoir is over 350 YJ. Current utilization of primarily the U-235 isotope consumes about 850 GW exergy. No commercial conversion of thorium currently exists.

In addition to heavy fissionable elements, there are a few select light nuclides that are able to undergo fusion at temperatures low enough to conceive of harnessing the energy they release in a controlled manner. The fusion cycle with the lowest ignition temperature involves deuterium and tritium, both isotopes of hydrogen. Deuterium exists in abundance in the ocean, but tritium does not exist naturally and must be bred from an isotope of lithium. With concentrated lithium occurrences of 14 Tg [46] and an isotope-averaged specific exergy of 226 TJ/kg lithium, the exergy reservoir for the deuterium–tritium cycle is approximately 3.1 YJ. Deuterium, the isotope of 1 in every 5000 hydrogen atoms [48], can be fused with another deuterium nucleus at

higher temperatures for a specific exergy of 345 TJ/kg. The resulting resource contained in the ocean is on the order of 10 million YJ.

6. Conclusions

Exergy is a useful tool for comparing resources with a diverse array of energy forms and quality. The varying degrees of thermal, chemical, nuclear, kinetic, radiative or gravitational potential energy contained in a resource are reduced to a single interchangeable currency. This perspective can serve as a starting place for technological or economic considerations of the usefulness of a resource.

Examining current resource utilization in the context of resource exergy can guide our efforts for technological research. In particular, the present low conversion efficiencies, small utilization, and enormous potential of the solar resource invite further study. In addition, estimates of the various untapped-but-large unconventional exergy resources such as clathrate hydrates and fusion nuclear cycles should also provide direction to the research community.

The known exergy reservoirs and flows within our sphere of influence are more than enough to provide energy services for the increasing population and activity of humankind. However, our present use of resources is on such a scale that it is no longer insignificant with respect to natural processes and exchanges, and may alter the state of the environment on which humans have come to depend. Energy concerns of the future will not focus on the amount of resources, but on the effect the manner of their use has on the non-linear global system we do not fully understand. It is therefore important to identify and assess a wide array of energy resources in order to provide enough energy options for a sufficiently sustainable energy future.

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Appendix A. Derivation of the intensive exergy of resources

A.1. Cosmic radiation exchange

Solar radiation reaches the Earth with an energy density of about 1368 W/m² and a spectral composition resembling blackbody radiation at 5800 K [49]. The exergetic portion of this energy flow can be modeled by assuming a blackbody absorbs this radiation and zero exergy heat from the environment and emits radiation characteristic of the ambient temperature [11,14]. Substituting expressions for blackbody radiation energy and entropy flows into the first term of Eq. (1) gives the ratio of radiation exergy to energy

$$\frac{\Psi_b}{\dot{E}_b} = 1 - \frac{4T_0}{3T} + \frac{1}{3} \left(\frac{T_0}{T} \right)^4, \quad (6)$$

where T is the blackbody temperature. For the solar blackbody temperature of 5800 K and an ambient temperature of 298 K, the ratio of exergy to energy from Eq. (6) equals 0.93.

The true solar radiation exergy value at the surface of the Earth depends on the spectral composition of solar energy due to selective frequency absorption in the atmosphere and the proportion of diffuse light. The change in exergy with natural changes in spectral composition is small, varying about 1.5% from solar zenith angle 0° to 75.5°, and can often be disregarded [50]. However, diffuse sunlight has a characteristic temperature of about 1600 K and corresponds to an exergy to energy ratio of about 0.75 [14]. The fraction of diffuse and direct sunlight can be added, weighted by the respective exergy-to-energy ratios to find the total solar radiation exergy.

The net exergy input due to radiation exchange between the Earth and space is the difference between the incoming extra-solar radiation and the outgoing infra-red radiation from the Earth. Both energy flows are non-equilibrium and require an exergy to energy relationship for arbitrary spectrum radiation [51]

$$\frac{\Psi_{ASR}}{\dot{E}_{ASR}} = 1 - \frac{4}{3} T_0 \left(\frac{\sigma}{\dot{E}_{ASR}} \right)^{1/4} + \frac{\sigma T_0^4}{3 \dot{E}_{ASR}}. \quad (7)$$

Incoming radiation is a composite of several low-energy density spectra that resemble blackbody radiation at 2.73, 20, 5000, and 20,000 K with an energy density of $12.5 \mu\text{W}/\text{m}^2$ [52]. With a calculated exergy to energy ratio of 10,600,000, the average exergy density of extra-solar radiation is $132 \text{ W}/\text{m}^2$. Radiation leaving the Earth carries exergy depending on the difference in energy flux between the observed long-wave infra-red energy and Planck emission from a body at the reference temperature. The average outgoing long-wave energy density varies with location from 100 to $300 \text{ W}/\text{m}^2$ [53] for an exergy density varying from 3 to $43 \text{ W}/\text{m}^2$ when the reference temperature is 289 K. Subtracting the global average $11 \text{ W}/\text{m}^2$ exergy density of the outgoing radiation from the incoming extra-solar radiation gives a net average exergy input of $121 \text{ W}/\text{m}^2$ at the outer edge of the stratosphere.

A.2. Wind and ocean currents

The exergy of fluid currents is entirely due to the kinetic energy of the fluid. The maximum work is extracted from a moving fluid when the velocity is brought to zero relative to the reference state. The kinetic energy of the fluid and its exergy have the same numerical value.

$$\Psi_{fluid} = \frac{1}{2} \rho V_0^3. \quad (8)$$

Wind, due to its variable nature, has specific statistical methods often used to describe the exergy flux at a site. Since the exergy flux depends on the power of the velocity, the average velocity does not describe the average exergy flux. It has been observed at many utilized and potential wind energy sites that the variation of wind speed closely follows a Weibull statistical distribution, described by a scale and shape parameter [19]. Other wind sites exhibit behavior better characterized by bi-modal or other statistical distributions. The site-specific extractable work can be described by a summation of a distribution of V_i^3 in place of the velocity term in Eq. (8).

A.3. Ocean surface waves

Wind blowing in one direction over a large body of water transfers energy to small surface irregularities, resulting in surface waves with increased gravitational potential energy. The waves concentrate kinetic energy transfer from the wind over many kilometers and can deposit this energy at the coastline. The primary factors determining the exergy of a fluid gravity wave are the period and amplitude [54]. For an approximately sinusoidal deep ocean wave, the length-specific exergy flux is

$$\Psi_{wave} = \frac{1}{2} \rho V g A^2, \quad (9)$$

where V is the wave speed and A is the amplitude.

Much like wind, ocean waves exhibit variability and superposition. If the water level of a certain area is known over a long period of time, statistical parameters can provide an average available energy from superimposed surface waves of arbitrary amplitude and period [22].

A.4. Precipitation

The specific exergy of precipitation can be broken down into physical and chemical components due to its gravitational and diffusive chemical potential energy relative to seawater. The physical exergy of a flowing body of water at the reference temperature and pressure is equivalent to its gravitational potential energy. The exergy associated with a steady-state flow of water is a straightforward relationship between the distance

above the reference height and flow rate. For a specific replenishing body of water such as a dammed reservoir, the gravitational potential exergy is

$$\Psi_{pot} = \dot{m}gz, \quad (10)$$

where \dot{m} is the mass flow rate, z is the vertical distance from the water level of the reservoir to the reference height or average sea level, and g is the gravitational constant.

Precipitation also contains a diffusive exergy component due to the difference in chemical potential between the Earth's freshwater and seawater. Since the difference between seawater and freshwater is primarily dissolved salts, this value can be computed most directly by considering a reversible osmosis process. The work done against the osmotic pressure is

$$\psi_{diff} = \frac{\Pi}{\rho_{seawater}} = -RT \ln(1 - y_{solute}), \quad (11)$$

where y is the mole fraction of solute in the water [55]. For the approximately 1.9 mol/kg ions dissolved in seawater at a salinity of 35 ppt [27], the diffusive exergy of freshwater is 4.9 kJ/kg.

A.5. Ocean thermal gradient

The exergy of the ocean thermal gradient derives from the difference in temperature between two thermal reservoirs. The physical exergy associated with flow between two large reservoirs of fluid at different temperatures is

$$\Psi_{TEG} = \dot{m}c_{p,avg}(T_w - T_c) \left(1 - \frac{T_c}{T_w}\right). \quad (12)$$

For a temperature difference of 20 K, the exergy content is approximately 7% of the thermal energy.

A.6. Tides

The maximum average power obtainable from a tidal energy site can be characterized by the gravitational potential of a designated water reservoir or area of ocean averaged over many tidal cycles. Exergy exists for both rising and falling tides. The specific tidal exergy of a designated area of ocean or enclosed reservoir is a function of the record of minima and maxima and the time periods between these levels. The lunar- and solar-induced rises in ocean level have different periods and are subject to orbit variations, as well as diffusing or concentrating effects of land and ocean floor topography [37]. As the tide rises and falls, an average exergy flow considering the reservoir area integrated over the height difference between local maxima and minima and the period between these points can be expressed as

$$\Psi_{tidal} = \frac{1}{n} \sum_n \frac{\rho g \int_{z_{n-1}}^{z_n} a_{reservoir}(z) dz}{t_n}, \quad (13)$$

where t is the period between local maxima and minima of the tidal record, a is the area of the reservoir at height z , and n is the index number for each maximum or minimum. This formula can be applied to an area of open ocean or a partially enclosed body of water such as a bay. The San Francisco Bay has an area of about 1200 km². The exergy associated with an average lunar semidiurnal tidal range of 2.5 m in the bay is about 1.4 GW.

A.7. Geothermal heat

Exergy from a geothermal resource is almost all physical. Hot, pressurized fluid or deep, hot rocks contain a substantial amount of thermal energy. Most authors prefer to describe the potential of a geothermal site by considering the properties of a pumped or natural fluid when it reaches the surface [56,57]. The thermal exergy of a compressible natural or working fluid at the wellhead can be expressed by the first

term of Eq. (1)

$$\psi_{geo} = [h - h_0 - T_0(s - s_0)]. \quad (14)$$

The chemical exergy associated with dissolved ions is almost always negligible relative to seawater. A representative brine at 436 K with a reference state temperature of 286 K has a specific exergy of 125 kJ/kg [41]. While straightforward, this formulation ignores the sustainability of the reservoir and subsurface heat transfer losses.

The renewable flux from these sources depends heavily on the rate the surrounding rocks or fluid can conduct or convect energy to a collector. A geothermal resource can only be considered renewable if its utilization allows a sustainable rate of exergy extraction and matter exchange. Reservoirs can experience a precipitous drop in temperature or fluid pressure if the energy or fluid removal rate is too high [58]. A sustainable rate can be estimated for conduction through hot, solid rock by solving the 3D conduction Poisson equation, modeling the geometry of the collector as cold sink. The estimation becomes more difficult when nearby convecting fluid or magma is involved. The fluid acts as an extended collector with flow rates that are difficult to quantify. Also, if fluid is removed from the reservoir, a mass balance must be achieved either by reinjection or natural replenishment of the reservoir.

A.8. Carbon-based fuels

The exergy derived from fossil reservoirs and biomass is primarily stored in the chemical energy of carbon-based molecules. We will assess exergy content by choosing reference products based on a chemical reaction with oxygen from the reference environment to form species in the reference state. The chemical composition of the fuel is therefore the primary factor in determining its exergy.

The chemical exergy calculation is straightforward if the entropy and enthalpy of the reactants are known. However, carbon-based fuels often contain a wide variety of species with complex bond interactions and unknown thermodynamic properties, making an exergy calculation based on reacting species impossible. Using Gibbs free energy relations, empirical data, and assuming the entropy of a fuel is equivalent to the sum of the entropies of the constituent elements, formulas have been developed for the chemical exergy of a fuel containing C, H, N, O, S and halogens [59,60]. These formulas permit calculation of the chemical exergy of a fuel based solely on its elemental analysis, or element mass fractions. The chemical exergy of a carbon-based fuel with an experimentally determined heat of combustion can be approximated by¹

$$\psi_{fuel} \approx 0.07075[C] - 24.15[H] + 4.328[O] + 7.060[S] - T_0[ash]s_{ash}^0 - \Delta_R h^0 \quad (15)$$

if the heat of combustion is known, or

$$\begin{aligned} \psi_{fuel} \approx & 32.90[C] + 2.040[N] + 117.7[H] + 16.34[S] - 13.41[O] - T_0[ash]s_{ash}^0 \\ & + 0.15[O][32.83[C] + 19.50[S] + 141.9([H] - [O]/8)] \end{aligned} \quad (16)$$

in MJ/kg if the heat of combustion is unknown, where the letters in brackets are the mass fractions of the corresponding elements and ash from an elemental analysis of the fuel. A representative value for the entropy of ash is 660 J/kg K [61]. Chemical exergies of carbon-based fuels often do not vary by more than 5% from the lower heating value [59]. In addition, the work potential associated with bringing the products to equilibrium with the environment is almost never utilized in practice. For these reasons, the heating value of carbon-based fuels is commonly used to describe its work value.

A.8.1. Conventional petroleum

Petroleum, containing hundreds of species interacting in a complex manner, is a good candidate for an elemental analysis approach to calculating chemical exergy. The constituent species include short alkanes, aromatics, and high molecular weight hydrocarbon chains. Though crude oil varies widely in composition, the

¹Coefficients are shortened from the original formulas to four significant figures.

carbon content by mass is usually from 0.83 to 0.87. Eq. (16) gives specific exergy values ranging from 40 to 44 MJ/kg for a variety of crude oil elemental compositions [62].

A.8.2. Unconventional petroleum and inorganic–hydrocarbon mixtures

Unconventional reservoirs of hydrocarbons include oil shale, tar sand, and pure heavy oil or bitumen. Oil shale and tar sand consist of heavy oil and/or bitumen mixed with various inorganic substances such as sand and carbonates. Heavy oil, bitumen, and the organic portions of the mixtures are high molecular weight hydrocarbons remaining after a conventional petroleum reservoir has degraded through weathering and bacterial conversion. Most of the lightweight paraffins are absent, leaving asphaltanes with high sulfur and metal content. Eq. (16) gives a chemical exergy of about 40 MJ/kg for representative elemental compositions of both heavy oil and bitumen [63,64].

The exergy of hydrocarbon–inorganic mixtures such as oil shale and tar sand is primarily contained in the chemical energy of the hydrocarbon portion. In addition to the hydrocarbon exergy, each type of constituent inorganic molecule has an exergy associated with the energy contained in chemical bonds, the concentration of the substance in the mixture, and the proportion of the constituent elements relative to the concentration of the representative species for these elements in the reference state. The exergy of the hydrocarbons in the mixture can be calculated using Eq. (16) as above if a mixture penalty is added that considers the mole fraction of the hydrocarbons in the mixture such as the second term of Eq. (3). The chemical and diffusive exergy of the inorganic portion can be calculated from standard exergy tables, but it is usually small and will not be considered in this study. Since the chemical exergy of the hydrocarbon portion is often around 40 MJ/kg, the specific exergy of the mixture will be primarily determined by the fraction of inorganic components. Under these assumptions, the composition of representative Estonian oil shale [65] and Hawkins, US tar sand [66] give calculated exergy values of 12 and 6 MJ/kg, respectively.

A.8.3. Coal

Coal consists of large, interconnected graphitic carbon structures and contains higher concentrations of metals and sulfur than other fossil fuels. Since there is no simple way to compute thermodynamic properties for these structures from a molecular point of view, we will also calculate the exergy of the coal reservoir using Eq. (16). We will use mass fractions from ultimate analyses of two representative coals, Blacksville bituminous and Absaloka subbituminous [67]. These compositions give specific exergy values of 29.81 MJ/kg bituminous and 19.87 MJ/kg subbituminous.

A.8.4. Natural gas

Unlike the previous fuels, the composition and interaction between species of conventional natural gas is simple enough to perform a straightforward chemical exergy calculation [5]. Natural gas is a widely varying mixture of low-mass hydrocarbons, nitrogen, and carbon dioxide with several other trace species. We find the exergy by summing the chemical exergy of each of the components for the reaction with oxygen



by the relation

$$\psi_{ch} = \sum \left\{ -\Delta_R g_{C_aH_b} + RT_o \ln \left[\frac{(y_{O_2,0})^{a+b/4}}{(y_{CO_2,0})^a (y_{H_2O,0})^{b/2}} \right] + RT_0 \ln y_{f,mix} \right\}, \quad (18)$$

where

$$\Delta_R g_{C_aH_b} = (a)g_{CO_2,0} + (b/2)g_{H_2O,0} - g_{fuel,0} - (a + b/4)g_{O_2,0}. \quad (19)$$

The second term of Eq. (18) quantifies the exergy associated with the concentration of the products relative to their atmospheric concentration $y_{x,0}$. The final term in Eq. (18) accounts for the concentration of the species within the gas mixture. Inert species such as nitrogen and carbon dioxide only contribute to the diffusive

exergy component. For a representative composition of natural gas [68] and a relative humidity of 80%, this analysis yields a specific exergy of 50.5 MJ/kg.

A.8.5. Methane clathrate

A large reservoir of exergy, considered unconventional by today's technological standards, is natural gas stored in clathrate hydrates. At near-freezing temperatures and pressures above atmospheric pressure, water can form crystalline structures encapsulating "guest" molecules of gas called clathrate hydrates. In the most common type of naturally occurring clathrate hydrate, one molecule of methane is trapped for every five molecules of water. Nearly pure methane clathrate hydrates dissociate when their temperature is raised to about 275 K or the pressure falls under 3 MPa [44]. Deposits are found either in the permafrost regions of continents or in sediment on the ocean floor. These underwater deposits are widely distributed throughout the coastal areas of every continent [69].

The exergy associated with natural clathrate hydrates is primarily due to the chemical exergy of the guest molecules. The crystalline structure has a dissociation energy that slightly reduces the net exergy value of the resource. The dissociation energy depends almost directly on the size of the guest molecule occupying the cavities and can be modeled or determined directly from T and P equilibrium data for a given clathrate hydrate using a derivative of the Clausius–Claypeyron equation

$$\frac{d \ln P}{d(1/T)} = \frac{-\Delta_D h^0}{ZR}, \quad (20)$$

where Z is the compressibility factor and $\Delta_D h^0$ is the dissociation energy of the clathrate [5]. The calculated specific exergy for representative methane clathrate hydrate found in the Mid-America Trench is 4.8 MJ/kg [44]. The guest molecules in this sample are mostly methane with about 85% water by mass.

A.8.6. Biomass

Harvesting biomass for energy conversion is a biological method for utilizing the solar radiation resource. Since biomass consists of long cellulose chains which are difficult to assign discrete thermodynamic properties, we will determine the chemical exergy of harvested biomass fuel in a manner similar to other carbon-based fuels of complex composition. Using elemental analyses and measured heating values in Eq. (15), Table 2 lists the specific exergies of several biomass samples on a dry basis [70].

Biomass consists mostly of celluloses, lignin, protein, and ash. Lignins, common in woody biomass, have a carbon content over 0.6 by mass with a specific exergy of about 25 MJ/kg, while celluloses have a carbon content from 0.40 to 0.45 and a specific exergy of 16–18 MJ/kg [28]. Ash, common in marine biomass, contributes very little energy and decreases the overall specific exergy.

A.9. Nuclear materials

The exergy of nuclear ore derives primarily from the strong nuclear force potential energy in the selected nuclides that this study presumes are available for fission or fusion. We will calculate the nuclear exergy of these species by assuming the energy equivalent of the mass defect between the products and reactants of a proposed nuclear reaction, not including the neutrino energy [6], is equal to the nuclear exergy as described in

Table 2
Specific exergy on a dry basis of representative biomass samples

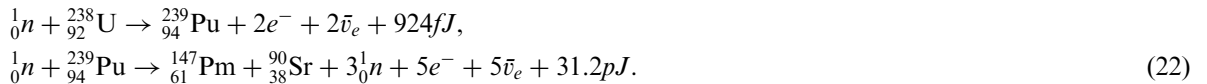
Biomass conversion feedstock	Specific exergy (dry) (MJ/kg)
Eucalyptus	19.9
Poplar	19.2
Corn stover	18.2
Bagasse	17.8
Water hyacinth	15.2
Brown kelp	10.9

Section 2.4. One can justify the approximation that nuclear binding energy release is effectively entropy free by considering the extreme temperature of the products of a nuclear reaction. The 650 billion K products of a typical fission reaction give an exergy-to-energy ratio indistinguishable from unity if the products are approximated as a perfect gas in equilibrium and the reference temperature is 289 K [5]. The chemical exergy of the inorganic substances in the ore and the necessary separation exergy are negligible compared to the nuclear exergy of the reacting nuclides and are not considered in this study.

Uranium has two isotopes, U-235 and U-238, found in a ratio of about 1:140 [48]. The fission of U-235 results in a double Gaussian distribution of fission products about the mass numbers 95 and 135, though these values are somewhat dependent on incident neutron energy [71]. The following representative reaction [72] gives an approximate nuclear exergy of 75 TJ/kg U-235.

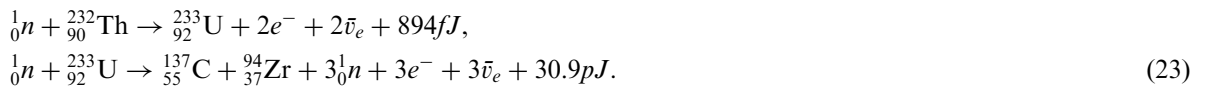


U-238 is not fissile, but can be transmuted to Pu-239 with fast neutron bombardment for a net energy release [72]



The fission of Pu-239 results in a fission products distribution similar to U-235. The above reaction gives a representative nuclear exergy of about 77 TJ/kg U-238. If we consider the uranium dissolved in seawater at a concentration of 3.3 ppb [49], we calculate a nuclear exergy of approximately 260 kJ/kg seawater, disregarding the relatively insignificant separation exergy.

Thorium is present in a single stable isotope that is not readily fissionable. However, Th-232 readily accepts a neutron and transmutes to fissile U-233, releasing energy [72]



The above reaction is representative, as U-233 has a spectrum of fission products much like the other uranium isotopes. Combining the above reactions gives a specific exergy of about 78 TJ/kg thorium.

Tritium, a commonly proposed fuel for fusion cycles because of its relatively low ignition temperature of 45 million K, does not occur naturally on the Earth's surface due to its 12-year half-life [48]. However, tritium can be produced by breeding it from lithium. Lithium has two stable isotopes, Li-6 and Li-7, with Li-6 making up 7.5% of natural deposits [48]. Tritium can be bred from Li-6 with a slow neutron and a net release of energy, but Li-7 requires a fast neutron and an overall energy input [72].



The nuclear exergy of lithium combined with far more common deuterium is 269 TJ/kg equimolar lithium–deuterium mixture for Li-6 and 162 TJ/kg for Li-7.

Fusion of solely deuterium requires confinement temperatures beyond our current technology, but would offer a nearly limitless supply of nuclear exergy considering the abundance of deuterium in the ocean. The cycle consists of four distinct reactions which can be combined as [72]



Deuterium has a nuclear exergy of 345 TJ/kg.

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